

was then removed by evaporation at 80 °C under reduced pressure. The residue was dried at 110°C for 12 hours. The temperature was then raised at a rate of 1 °C/min to 250 °C. This temperature was maintained for 2 hours and then raised by 3 °C/min to 550 °C. The final step was a calcination step at 550 °C for 8 hours under an air atmosphere.

Catalysts with different tungsten metal loadings were prepared i.e. 3, 4.5, 6, 7, 8, 10, 15 and 20 wt% of WO₃ on SiO₂. These catalysts are characterised in Table 1.

Table 1

Catalyst	Actual Composition (wt% WO ₃)	Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Avg. Pore Size (nm)	Crystallite Size (Å)
3%WO ₃ /SiO ₂	2.8	326	1.11	13.7	N/A
4.5%WO ₃ /SiO ₂	4.1	324	1.16	14.1	N/A
6%WO ₃ /SiO ₂	5.5	312	1.12	14.1	N/A
7%WO ₃ /SiO ₂	6.8	287	1.04	14.0	N/A
8%WO ₃ /SiO ₂	8.0	252	0.98	15.6	126.0
10%WO ₃ /SiO ₂	9.9	276	0.99	13.9	134.1
15%WO ₃ /SiO ₂	14.2	267	0.96	14.0	141.3
20%WO ₃ /SiO ₂	19.7	234	0.85	14.2	151.0

Optimisation of a metathesis catalyst using 1-octene as a representative feed stream:

Table 2 gives a summary of the conversions and product selectivities obtained with WO₃/SiO₂ metathesis catalysts with different WO₃ loadings using 1-octene as feed. All reactions were on-line for 8 hours and results are reported as averages over the 8-hour period. Reaction conditions were 460 °C, 5.6 h⁻¹ LHSV and atmospheric pressure.

Table 2

WO₃ Loading/%	3	4.5	6	7	8	10	15	20
C ₈ Conversion/%	56.8	78.9	88.6	87.1	88.4	88.3	88.3	88.4
Selectivity C ₁₄ Linear/%	15.2	7.3	5.3	4.8	4.6	4.2	4.0	4.0
Selectivity C ₁₄ Branched/%	0.6	0.5	0.5	0.5	1.0	0.9	0.9	0.8
Selectivity C ₉₋₁₃ Linear/%	46.4	47.7	45.5	44.0	40.0	40.7	40.0	39.5
Selectivity C ₉₋₁₃ Branched/%	1.6	2.2	2.6	2.7	5.7	5.8	5.4	5.3

- 5 Graph 1 shows the relationship between WO₃ loading and C₈ conversion. It can be seen from Graph 1 that that WO₃ loading of more than about 6% wt% provides no significant increase in conversion.

- Graph 2 shows the relationship between conversion and time (hours) for catalysts with different WO₃ loadings. It can be seen from Graph 2 that catalysts having a WO₃ loading of less than about 4.5% wt% experience significant poisoning.

- 15 These results indicate an optimum WO₃ loading where selectivity to linear metathesis products is high, branched product formation is relatively low and catalyst lifetime is high. This optimum appear to be in the region of between 6 and 8wt%WO₃.

- 20 Graph 3 shows the effect of the variation of the pH during impregnation on catalyst selectivity towards primary metathesis products.

- 25 Tunnelling electron microscope analysis showed improved dispersion of WO₃ on the carrier with catalysts prepared with an aqueous solution at a high pH (pH10-12). More crystallites and an even or, in other words, uniform dispersion over the silica carrier was observed at a higher pH impregnation and Table 3 gives crystallite size determinations.

Table 3

Catalyst	pH of impregnation solution	Crystallite Size (Å)
8%WO ₃ /SiO ₂	1	260.0
8%WO ₃ /SiO ₂	5	126.0
8%WO ₃ /SiO ₂	12	110.0

Table 4 gives a summary of the conversions and product selectivities obtained with WO₃/SiO₂ metathesis catalysts prepared by impregnating a silica carrier at different pH's, using 1-octene as feed. Impregnation at a higher pH resulted in increased production of linear metathesis products. The largest improvement was observed with the production of the primary linear C₁₄ metathesis product. The linear secondary metathesis products also show an improvement with a higher pH. The reduction in branched metathesis products can be attributed to poisoning of some of the Brønsted acidity necessary for skeletal isomerisation due to the basic environment during preparation.

Table 4

pH	1	3	5	8	10	12
Conversion/%	88.5	88.7	88.2	88.2	87.6	85.5
C ₉ -C ₁₃ Branched	1.9	1.8	1.8	1.8	1.7	1.3
C ₉ -C ₁₃ Linear	46.0	45.3	46.5	45.6	48.7	49.0
C ₁₄ branched	0.3	0.3	0.3	0.3	0.3	0.2
C ₁₄ linear	5.3	5.3	5.3	5.4	6.0	8.2

An example of using the optimised catalyst in a metathesis process using a feed stream of 1-heptene:

Scheme 1 shows a plant equipped with the necessary work-up facilities and recycle lines for metathesis.

Column 1 includes a reboiler set at 220 °C, Column 2 includes a condenser set at 25 °C and Reboiler set at 34 °C. The Recycle line is set at 25 °C, and the Reactor temperature is 460 °C. The LHSV is 16 h⁻¹ (including a recycle loop of C₅ – C₁₀ at a 1:5.6 ratio) and the Reactor pressure is 10 kPa_g, thus

dodecene, olefins formed outside this range can be referred to as secondary metathesis products. This value gives an indication of the ratio between isomerization of feed/product and metathesis on the catalyst surface.

5 **Table 6**

	Run 1	Run 2
Online time (hours)	700	1200
Total feed conversion (%)	88.2	84.7
Selectivity (%) to:		
Ethylene	7.56	8.52
Propylene	4.74	4.05
Undecene (C ₁₁)	12.03	12.81
Dodecene (C ₁₂)	41.28	46.25
Tri- and Tetradecene (C ₁₃ – C ₁₄)	7.62	5.55
Ethylene Purity (%) ^a	98.92	99.27
Propylene Purity (%) ^b	98.85	98.97
Linearity of C ₁₂ (%)	97.0	97.0
% Primary metathesis ^c	65.3	66.6
Mass Balance (%)	89.4	95.1

The values of the two runs depicted in Table 6 are very similar. There was however a slight drop in conversion with the regenerated catalyst, but the selectivity towards the detergent range C₁₁ and C₁₂ increased with the regenerated catalyst.

The high linearity index of the dodecene is advantageous for example used in detergent synthesis. For linear alkyl benzenes synthesis the dodecene should be highly linear.

Optimising the above example process using, as an example, a feed stream of 1-heptene:

By using the abovementioned optimised catalyst together with the optimised conditions the applicant managed to keep the catalyst on-line for 1200 hours without losing any significant activity or any significant indication of catalyst deactivation. The catalyst is therefore capable of running for longer than 1200 hours. Prior art work done on short-chain olefins (C₂-C₄) only managed a

Table 7

Catalyst	8%WO ₃ /SiO ₂	6% WO ₃ /SiO ₂
LHSV	16	16
Conversion/%	54.2	71.3
Selectivity C ₉ -C ₁₃ Branched/%	1.9	1.8
Selectivity C ₉ -C ₁₃ Linear/%	47.6	47.3
Selectivity C ₁₄ Branched/%	0.2	0.2
Selectivity C ₁₄ Linear/%	14.7	15.2
% Branched C ₉ -C ₁₃	4.1	3.9
% Branched C ₁₄	1.4	1.4